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1. REPORT DATE (DD-MM-YYYY) 25-03-2007		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 01-03-2004 – 30-11-2007	
4. TITLE AND SUBTITLE Experimental and Theoretical Investigation of Collisional Energy Transfer in Free Radicals of Atmospheric Importance				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-04-1-0152 / FA9550-04-1-0103	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Millard H. Alexander and Paul J. Dagdigan				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The University of Maryland Department of Chemistry and Biochemistry College Park, MD 20742-2021 The Johns Hopkins University Department of Chemistry Baltimore, MD 21218-2685				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 4015 Wilson Boulevard Rm 713 Arlington, VA 22203-1954 <i>Dr Michael Berman</i>				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Collisional relaxation of the atmospherically important free radicals OH and NO by open-shell atoms have been studied in a coordinated theoretical and experimental investigation. A quantum statistical method has been employed to describe collisional processes proceeding through a strongly bound collision complex, such as occur in the interaction of many free radicals with atoms. This theory has been used to compute rotationally and vibrationally inelastic collision rates for collisions of OH with H atoms. Similar calculations for collisions on the lowest $^2A'$ and $^2A''$ potential energy surfaces for OH-O collisions have been carried out, with good agreement with the accompanying experiments. In these experiments, the rate constants for total removal of OH($v=1$) molecules by O(3P) and N(4S) atoms have been measured in a discharge-flow experiment. Rate constants for OH($v=1$) were found to be 1.1 ± 0.1 and 1.6 ± 0.4 times the corresponding O($v=0$) rate constant. A method for the absolute measurement of O(3P) atoms by cavity ring-down spectroscopy on the forbidden $^1D_2 \leftarrow ^3P_2$ line has been developed and validated. Electronic quenching of OH($A^2\Sigma^+$) has also been investigated theoretically. Finally, simulations of Al atoms doped in liquid helium have been carried out to compute the spectrum of the doped atom, and the recombination of Al atoms in solid H ₂ has been investigated theoretically.					
15. SUBJECT TERMS Molecular free radicals, hydroxyl, nitric oxide, collisional energy transfer, vibrational relaxation, electronic quenching					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 14	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED			19b. TELEPHONE NUMBER (include area code)

**EXPERIMENTAL AND THEORETICAL INVESTIGATION
OF COLLISIONAL ENERGY TRANSFER IN FREE RADICALS
OF ATMOSPHERIC IMPORTANCE**

FINAL REPORT

March 1, 2004 – November 30, 2007

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Air Force Office of Scientific Research

Grant Number FA9550-04-1-0152 (The University of Maryland)

Grant Number FA9550-04-1-0103 (The Johns Hopkins University)

20080118127

TABLE OF CONTENTS

	page
I. Summary of Work and Description of Work Accomplished	1
A. Theoretical Investigation of Collisions of a Free Radical With an Open-Shell Species	1
B. Experimental Investigation of Collisional Relaxation of Vibrationally Excited OH and NO by Open-Shell Atoms	2
C. Investigation of Electronic Quenching of $\text{OH}(A^2\Sigma^+)$ in Collisions with Molecular Hydrogen	5
D. Determination of $\text{O}(^3P)$ Atom Concentrations by Cavity Ring-Down Spectroscopy on the Forbidden $^1D_2 \leftarrow ^3P_2$ Line	5
E. Simulations of Al Atoms Doped in Liquid Helium	7
F. Recombination of Al Atoms in Solid Hydrogen	8
G. Investigation of Non-Adiabaticity in the $\text{F} + \text{HCl} \rightarrow \text{HF} + \text{Cl}$ and $\text{O}(^3P) + \text{H}_2 \rightarrow \text{OH} + \text{H}$ Reactions	9
II. References	11
III. List of Publications Prepared under AFOSR Grant Nos. FA9550-04-1-0152 and FA9550-04-1-0103	13
IV. List of Participating Scientific Personnel	14

I. SUMMARY OF WORK AND DESCRIPTION OF WORK ACCOMPLISHED

This project has involved the closely coordinated theoretical and experimental investigation of the collisional relaxation of the molecular free radicals OH and NO by open-shell atoms. These species are generated in high vibrational and rotational levels in the mesosphere and lower thermosphere through highly exothermic reactions, *e.g.* $N(^2D) + O_2$ and $H + O_3$. The atmospheric signatures of these and other molecules are strongly influenced by the subsequent redistribution of this energy. While there has been considerable study of the relaxation of OH and NO by stable molecules, our knowledge of their relaxation by open-shell atoms, notably $O(^3P)$, prior to this work was quite limited.

Efforts under this project have mainly focused on the study of collisional relaxation of OH and NO by open-shell atoms, in particular $O(^3P)$. The sections below summarize the accomplishments of this project, as well as describe work initiated with earlier support under the HEDM program. For administrative reasons, the collaboration between Alexander and Dagdigian was supported by two separate grants, one to the University of Maryland and one to The Johns Hopkins University.

A. Theoretical Investigation of Collisions of a Free Radical with an Open-Shell Species

A statistical model, originally developed by Rackham and Manolopoulos^{1,2} to describe chemical reactions proceeding through a strongly bound collision complex, has been applied to the collisional relaxation of a free radical by an open-shell species. In such a collision, at least one of the potential energy surfaces possesses a deep well corresponding to the stable molecule which can be formed by recombination of the open-shell species. The inelastic scattering dynamics is treated by coupled-states capture theory with inclusion of all the relevant potential energy surfaces and the couplings between them. Specifically, we have shown how to introduce the coupling between the nuclear and electronic degrees of freedom of a molecule in a $^2\Pi$ electronic state..

We have used this approach to investigate the inelastic scattering of OH by H .³ Since the $O(^1D) + H_2$ reaction is exothermic, at energies below the $O(^1D) + H_2$ channel threshold capture (from $OH + H$) into the H_2O complex can lead only to release of OH in a different vibration-rotation state. The overall inelastic scattering can be divided into a direct component due to

coupling between, and the anisotropy of, the repulsive potentials which correlate with $\text{OH} + \text{H}$ and a capture component, due to the capture-release mechanism discussed above.

Our calculations³ show that rotationally inelastic scattering [$\text{OH}(j) + \text{H} \rightarrow \text{OH}(j') + \text{H}$] is dominated by direct scattering and is similar in magnitude and dependence on final quantum number of the rotationally inelastic scattering of OH by He or H_2 . However, for vibrational relaxation the capture mechanism dominates and results in vibrationally inelastic cross sections which are not insubstantial. This confirms an earlier conjecture by Smith⁴ of complex-mediated vibrational relaxation. In addition, we predict the same final-state OH A'/A'' propensities seen in our theoretical simulations of the $\text{O} + \text{H}_2$ reaction,⁵ as well as in the earlier experimental work of Wiesenfeld, Butler, Gericke, and their co-workers.^{6,7}

Potential energy surfaces (PESs) for the interaction of OH with $\text{O}(^3P)$ atoms have also been computed.⁸ Both the lowest $^2A'$ and $^2A''$ potential energy surfaces have a barrierless access to a well. In contrast to the $\text{O}(^1D) + \text{H}_2$ reaction, here the $\text{H} + \text{O}_2$ channel is lower in energy than the $\text{OH} + \text{O}$ asymptote. Consequently, the complex-mediated process $\text{OH}(v=1) + \text{O} \rightarrow \text{OHO}^\ddagger \rightarrow$ products pathway leads to removal of the vibrationally excited level primarily by production of $\text{H} + \text{O}_2$ products. Rate constants have been computed using statistical, coupled-states calculations² for collisions on the $^2A'$ and $^2A''$ potential energy surfaces, separately. Overall good agreement was seen between the calculated thermal vibrational relaxation rate constant at 300K and the value measured in Dagdigians's laboratory,⁹ which is discussed in the next section. However, for the $\text{OH}(v=0) + \text{O} \rightarrow \text{H} + \text{O}_2$ reaction a comparison between the statistical, coupled-states integral cross sections and the more exact, full reactive scattering calculations of Honvault and Guo,¹⁰ indicates that the statistical method overestimates the reactive cross section by at least a factor of 50%. We are currently continuing our theoretical investigation of this reaction.

B. Experimental Investigation of Collisional Relaxation of Vibrationally Excited OH and NO by Open-Shell Atoms

Knowledge of rate constants for collisional relaxation of the internal degrees of freedom of the OH and NO radicals are important for an understanding of the IR atmospheric emissions of these species. While there has been considerable study of relaxation rates by stable, closed-shell collision partners, only a few investigations of collisions with open-shell species have been carried out. We have carried out experimental studies of the collisional vibrational relaxation of

OH($v=1$) by O(3P)⁹ and N(4S)¹¹ atoms and have investigated the collisional vibrational relaxation of NO by oxygen atoms.

Hydroxyl radicals in the ground $v=0$ vibrational level can react with both O(3P) and N(4S) atoms, to yield O₂ and NO molecular products, respectively, and OH($v=1$) can be removed by both reaction and vibrational relaxation. For both atomic species, collisional removal of OH($v=1$) is mediated by formation and decay of a transient complex (HO₂ and HNO, respectively). Our experiment employs a discharge-flow apparatus, in which O(3P) or N(4S) atoms are prepared by microwave discharge in an O₂/Ar or N₂/Ar mixture, respectively. A photolytic precursor is added upstream of a laser-induced fluorescence detection port, and OH is generated by 193 nm photolysis of a suitable precursor (>95% H₂O₂). We had considered the use of the commonly employed OH precursor HNO₃, but 193 nm photolysis produces some O(1D)¹² and complicates the relaxation kinetics by its reaction with the precursor to yield OH in several excited vibrational levels. OH($v=0$ and 1) concentrations were monitored by laser-induced fluorescence as a function of time after the photolysis laser pulse. Photolysis of H₂O₂ yields mainly OH($v=0$) and ~1% OH($v=1$),¹³ and possible cascade contributions from higher OH vibrational levels are avoided.

In these experiments, the concentration of the atoms was determined from the decay rate of the OH($v=0$) concentration when the microwave discharge is on. This is a reasonable approach for the measurement of the atom concentrations since the rate constants for the OH($v=0$) + O(3P) → H + O₂ and OH($v=0$) + N(4S) → H + NO reactions are known from previous work.^{14,15} In effect, we are comparing the collisional removal of OH($v=0$ and 1) under the same conditions in order to determine the enhancement of the removal rate with vibrational excitation. In extracting the total rate constants for removal of OH($v=1$) in collisions with the atoms, we must also take into account vibrational relaxation of OH($v=1$) by H₂O₂ and other species. In the case of collisions with O(3P), we found that the concentration of the H₂O₂ precursor in the flow, as gauged by the OH($v=0$ and 1) laser-induced fluorescence signals, was reduced by a factor of ~3 when the microwave discharge is turned on. This results from a slow chain reaction involving O(3P), HO₂, OH, and H radicals which consumes H₂O₂. We simulated this decomposition by kinetic modeling in order to estimate species concentrations in the low with the microwave discharge on and hence O(3P) atoms present. In the case of OH–O collisions, we determined that the ratio of the room-temperature total removal rate constant for

OH($v=1$) to that for OH($v=0$) was 1.1 ± 0.1 . Thus, the removal rate for OH($v=1$) is found to be slightly larger than for OH($v=0$), but the difference is within the experimental uncertainty.

Schatz and co-workers¹⁶ carried out an extensive *ab initio* study of the PESs connecting the OH + N and H + NO channels, and the higher-energy O + NH asymptote. The OH + N reagents can react on a $^3A''$ PES to form a HON complex, which can isomerize to form HNO and then dissociate to H + NO products. Unfortunately, they did not explore the dependence of the $^3A''$ PES upon the O–H separation. Following on our study of OH($v=1$)–O collisions, we studied the effect of vibrational excitation on the total removal rate of OH($v=1$) by N(4S) atoms.¹¹ In this system, the OH concentration was unaffected by the presence or absence of N(4S) atoms. For this system, we found that the ratio of the room-temperature total removal rate constant for OH($v=1$) to that for OH($v=0$) was 1.6 ± 0.4 . Hence, there is a significant enhancement in the removal rate with vibrational excitation in this system.

We also investigated the vibrational relaxation of OH($v=1$) by H atoms, which were prepared by a microwave discharge of H₂. In this case, the OH concentrations were reduced by a factor of ~ 10 when the discharge was turned because of a chain reaction of the precursor H₂O₂ with H atoms, much greater than was the case for O(3P) atoms. The greater efficiency of removal of H₂O₂ by H atoms is consistent with our kinetic modeling of the destruction of H₂O₂. Because of the significant destruction of H₂O₂ by H atoms, a reliable rate constant for the collisional removal of OH($v=1$) by H atoms could not be determined.

We also carried out an experimental study of collisional vibrational relaxation of NO by O(3P) atoms. The NO(v) concentration is followed as a function of time after the 193 nm photolysis of *t*-butyl nitrite precursor by laser-induced fluorescence detection in the NO A – X band system. In this experiment, the oxygen atom concentration is determined by cavity ring-down spectroscopy on the forbidden $^1D_2 \leftarrow ^3P_2$ line, as described in detail in Sec. D. With this concentration measurement, the pseudo first-order NO(v) decay rate can be converted to a bimolecular rate constant, after correction for other (small) loss processes. A preliminary value of $(2.86 \pm 0.61) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained for the relaxation of NO($v=2$) by O(3P) atoms. This value falls in the lower range of recent measurements of the room-temperature vibrational relaxation rate constants of NO($v=1$ and 2) by oxygen atoms.

C. Investigation of Electronic Quenching of OH($A^2\Sigma^+$) in Collisions with Molecular Hydrogen

In a collaborative project with the Lester group at the University of Pennsylvania, we carried out theoretical calculations to help understand the experimental investigation of the inelastic scattering channel resulting from electronic quenching of OH $A^2\Sigma^+$ by molecular hydrogen (also supported by AFOSR under grant FA9550-04-1-0068). The experiments utilized a pump-probe scheme to determine the OH $X^2\Pi$ population distribution following collisional quenching in a pulsed supersonic expansion.^{17,18} The experiments revealed a high degree of rotational excitation (N'') of the quenched OH $X^2\Pi$ products observed in $v''=1$ and 2, as well as a pronounced propensity for quenching into the $\Pi(A')$ Λ -doublet level. To supplement these experiments, we carried out extensive multi-reference, configuration-interaction calculations aimed at exploring the topology of the relevant potential energy surfaces. Electronic quenching of OH $A^2\Sigma^+$ by H_2 proceeds through conical intersections between two potentials of A' reflection symmetry (in planar geometry) that correlate with the electronically excited $A^2\Sigma^+$ and ground $X^2\Pi$ states of OH. The conical intersections occur in high-symmetry geometries, in which the O-side of OH points toward H_2 . Corroborating earlier work of Hoffman and Yarkony,¹⁹ our calculations revealed a steep gradient away from the OH- H_2 conical intersection as a function of both the OH orientation and interfragment distance. The former is responsible for the high degree of rotational excitation observed for the quenched OH $X^2\Pi$ products. In addition, because a third PES of A'' reflection symmetry, correlating with OH $X^2\Pi + H_2$, does not have this pronounced angular gradient, coplanar passage through the conical intersection should favor the observed Λ -doublet propensity. In addition, we predict that, as the quenched products separate, adiabatic relaxation of the H_2 stretch will be incomplete, leading to substantial vibrational excitation of the H_2 products subsequent to the electronic quenching of OH.

D. Determination of O(3P) Atom Concentrations by Cavity Ring-Down Spectroscopy on the Forbidden $^1D_2 \leftarrow ^3P_2$ Line

Oxygen atoms are important in many environments, including combustion media, plasmas, and the atmosphere. The availability of a non-intrusive spectroscopic method for the determination of O(3P) atom concentrations is highly desirable. We desire such a method in our collisional relaxation experiments. The measurement of rate constants for collisional energy transfer in free radicals induced by oxygen atoms entail measurement of the decay rates of the

free radical concentration under pseudo first-order conditions, *i.e.* with the oxygen atoms in excess. The desired bimolecular rate constants can then be calculated by dividing the decay rates by the oxygen atom concentration.

Several spectroscopic methods have previously been employed to determine O(3P) atom concentrations. The strong $3s\ ^3S \leftarrow ^3P$ resonance transition near 130 nm has been extensively employed in discharge-flow experiments²⁰ but is limited to low concentrations and cannot be applied to flames etc. Two-photon fluorescence excitation²¹ near 226 nm to the $3p\ ^3P$ state and detection of near IR $3p\ ^3P \rightarrow 3s\ ^3S$ emission circumvents problems with VUV spectroscopy; however, this approach requires consideration of electronic quenching, energy transfer, stimulated emission, and ionization, as well as requiring independent calibration.²²⁻²⁴

We have shown that the use of cavity-ring down spectroscopy (CRDS)^{25, 26} on the forbidden $^1D_2 \leftarrow ^3P_2$ line at 630 nm can be employed for the non-intrusive spectroscopic determination of O(3P) atom concentrations.²⁷ This magnetic dipole transition has a recommended²⁸ spontaneous emission probability of $5.63 \times 10^{-3}\ \text{s}^{-1}$, which implies a peak absorption cross section of $5.71 \times 10^{-22}\ \text{cm}^2$ for a room-temperature Doppler-broadened line profile, or an integrated absorption cross section of $2.93 \times 10^{-23}\ \text{cm molecule}^{-1}$. In CRDS, absorption is detected by a increase in the rate of decay of light injected into an optical cavity containing the sample.

We have applied CRDS to detect O(3P) atoms in a discharge-flow apparatus. Oxygen atoms were generated by passing a N₂O/Ar mixture or pure O₂ through a 2450 MHz microwave discharge. The effluent from the discharge passed through a 104 cm long optical cavity, 83 cm of which contained O(3P) atoms. The CRD mirrors have 99.99% reflectivity, which led to a empty-cavity photon decay lifetime of $\sim 35\ \mu\text{s}$. In order to take account of the fact that our laser linewidth ($0.15\ \text{cm}^{-1}$ FWHM) was greater than the O atom Doppler width ($0.05\ \text{cm}^{-1}$ FWHM), integrated O atom absorbances were determined by scanning over the line. We found that O(3P) atom concentrations in the $10^{14}\ \text{cm}^{-3}$ range could be measured to an accuracy of $\sim 4 \times 10^{13}\ \text{cm}^{-3}$.

There is an uncertainty of only 8% in the transition probability for the $^1D_2 \leftarrow ^3P_2$ line,²⁸ and hence a similar uncertainty in the absorption cross section. We checked the accuracy of our CRDS measurements by comparison concentrations determined by this technique and by the established method of titration with NO₂ and found good agreement between the two methods.

We are currently employing this method to determine $O(^3P)$ atom concentrations in our ongoing study of the vibrational relaxation of $NO(v)$ by $O(^3P)$ atoms, as mentioned above.

E. Simulations of Al Atoms Doped in Liquid Helium

We described for publication the results of a path-integral, Monte-Carlo simulation of the spectrum of a single Al atom doped into liquid helium clusters.²⁹ For this system high-resolution spectra at 0.38K have been recorded by Lehmann, Scoles, and coworkers, with AFOSR HEDM support.³⁰ The helium environment is unique because the interaction between helium atoms is very weak. Because of the large zero-point motion, helium clusters are known to be the only clusters that remain liquid under all conditions of formation.³¹ Although the spectra of alkali atoms in helium droplets have been investigated theoretically by density functional methods (Cs) and path-integral Monte-Carlo simulations (Li, Na, K),^{31,32} our work is the first attempt to perform similar simulations for group IIIa atoms.

Following earlier work in our group,³³⁻³⁶ we used *ab initio* Al-He pair potentials for the ground and lowest excited Al-He electronic states, within a Balling and Wright pairwise Hamiltonian model,³⁷ to describe the interaction between the open-shell Al atom and an arbitrary number of He atoms. By describing this interaction as a sum of pairwise 6×6 Hamiltonian matrices, rather than the sum of pairwise scalar potentials, we can treat accurately the electronic anisotropy of the Al atom. A similar approach is used to describe the interaction of Al in its excited 3*d* and 4*p* states with multiple He atoms.

In our simulation of the arrangement of He atoms around a single Al atom doped in a He cluster, we used a multilevel Monte-Carlo scheme to minimize the computational effort. This involves first performing large coarse displacements of the system in configuration space, and then refining only if the initial displacement is accepted, an adaptation of the bisection algorithm of Ceperly and co-workers.³⁸ The simulation of the absorption spectra was done using a semiclassical Franck-Condon approximation.^{39,40}

Our calculations reveal that the doping of the Al 3*p* electron strongly influences the He packing. With inclusion of tail corrections for the ground and excited states potentials, our calculated 3*d*←3*p* spectrum agrees reasonably well with the experimental spectrum reported by Lehmann, Scoles, and co-workers.³⁰ The blue shift of the calculated spectrum associated with the 4*s* ← 3*p* transition of solvated Al is about 25 nm ($\sim 2000\text{ cm}^{-1}$) larger than seen in

experiments on Al embedded in bulk liquid He.⁴¹ We also predict that the spectrum associated with the $4p \leftarrow 3p$ transition will be blue shifted by $\sim 7000 \text{ cm}^{-1}$ (nearly 1 eV).

F. Recombination of Al Atoms in Solid Hydrogen

The embedding of light impurities in solid hydrogen has received considerable experimental and theoretical attention in recent years, partly because of the potential technological applications as high energy density materials.⁴² In collaboration with the Voth group at Utah, we have published several earlier investigations of a single B³⁵ or Al³⁶ atom embedded in solid *para*-H₂. We found that in both cases the dependence of the atom-*p*H₂ potential on the orientation of the singly-filled *p* electron induces some distortion of the nearest-neighbor ligand shell to allow the *p*-orbital to orient itself to minimize the repulsive Σ and maximize the attractive Π interactions.

For open-shell atoms such as B and Al, one important question remains unanswered: when doped with multiple atomic impurities, is the system stable with respect to recombination, a highly exothermic process? To study more than one doped open-shell atom, we must consider the interaction between impurity atoms, which depends on the relative orientation of the *p*-electrons of both dopants. In an earlier article we developed a theoretical framework for the accurate description of the interaction of two ²*P* atoms in the presence of multiple spherical ligands.⁴³

With this potential, we developed⁴⁴ a simple approach to investigate the likelihood of recombination: We place the two Al atoms at several initial substitution sites, similar to those chosen in our earlier paper.⁴³ We then allow the separation vector for the two Al atoms to decrease. At each reduced value of this separation coordinate, which we keep fixed, we then perform path-integral, Monte-Carlo calculations to sample the motion of the *p*H₂ molecules. From the results of these PIMC simulations we can determine the average energy, as a function of the Al–Al distance. Since the Al atoms are ~ 13 times heavier than a *p*H₂ molecule, this average energy will provide, in a Born-Oppenheimer sense, the effective potential energy for motion of the Al atoms along the recombination coordinate. If a potential barrier exists, we can then use standard transition state theory to estimate the lifetime against recombination. This approach allows the investigation of atomic recombination in solids when quantum effects are substantial.

For substitution sites within a distance of ~ 13 bohr, we found that the two Al atoms greatly distort the lattice structure to allow recombination into the Al_2 molecule.⁴⁴ This releases a large amount of energy. This result is different from the model studies presented in a previous paper, where the $p\text{H}_2$ molecules were fixed in place. It is the quantum nature of the $p\text{H}_2$ molecules that facilitates recombination of the Al atoms. However, when the two Al atoms are embedded initially at distances longer than ~ 14 bohr, the equilibrated separation between the two Al atoms is little changed from the initial substitutional sites. The interaction between the two Al atoms is small, and the Al atoms affect the system separately.

This observation from our simulations provides a bound to the maximum concentration to which Al atoms could be doped into solid $p\text{H}_2$, without recombination. We estimate that recombination will occur for molar ratios greater than 1 Al : 15 H_2 , or 0.0667 mole percent. From a straightforward application of simple transition state theory, we estimated the lifetime of the embedded solids at $T = 4$ K to range from minutes to days.⁴⁴

G. Investigation of Non-adiabaticity in the $\text{F} + \text{HCl} \rightarrow \text{HF} + \text{Cl}$ and $\text{O}(^3P) + \text{H}_2 \rightarrow \text{OH} + \text{H}$ Reactions

Millard Alexander supervised Michael Deskevich, a graduate student at the University of Colorado, in the determination of the coupled electronic potential energy surfaces for the $\text{F} + \text{HCl} \rightarrow \text{HF} + \text{Cl}$ reaction. This reaction is under ongoing experimental investigation in the group of David Nesbitt. With the goal of future scattering calculations to compare with these experiments, it is necessary to transform the three electronically adiabatic potential energy surfaces (two of $^2A'$ symmetry and one of $^2A''$ symmetry) into a quasi-diabatic representation. This is entirely analogous to our earlier treatment of the $\text{F} + \text{H}_2$ reaction dynamics.⁴⁵ Our expertise in the determination of the potential energy surfaces for the $\text{F} + \text{H}_2$ reaction, as well as for the $\text{O}(^3P) \cdots \text{H}_2$ complex⁴⁶ (the latter projected completed with the support of an earlier AFOSR grant), proved invaluable in mentoring Mr. Deskevich.

We also extended this past project to the determination of the full, coupled potential energy surfaces for the $\text{O}(^3P) + \text{H}_2 \rightarrow \text{OH} + \text{H}$ reaction. Here, there are two potential energy surfaces of $^2A''$ symmetry and one of $^2A'$ symmetry. In contrast to the $\text{F} + \text{H}_2$ reaction, two of these surfaces lead, over a high barrier, to reaction, while one is repulsive. Schatz and co-workers⁴⁷ had shown that the crossing with the singlet potential energy surfaces which emanate from the higher $\text{O}(^1D) + \text{H}_2$ occur beyond the barrier on the triplet potential energy surfaces. It

is our goal to carry out a fully-quantum, multiple-potential-energy surface study of the $\text{O}(^3P) + \text{H}_2 \rightarrow \text{OH} + \text{H}$ reaction, similar to our earlier studies of the $\text{F} + \text{H}_2$ and $\text{Cl} + \text{H}_2$ reactions.^{45,48}

II. REFERENCES

1. E. J. Rackham, F. Huarte-Larranga, and D. E. Manolopoulos, *Chem. Phys. Lett.* **343**, 356 (2001).
2. E. J. Rackham, T. Gonzalez-Lezana, and D. E. Manolopoulos, *J. Chem. Phys.* **119**, 12895 (2003).
3. S. Atahan and M. H. Alexander, *J. Phys. Chem. A* **110**, 5436 (2006).
4. I. W. M. Smith, *Chem. Soc. Rev.* **14**, 141 (1985).
5. M. H. Alexander, E. J. Rackham, and D. E. Manolopoulos, *J. Chem. Phys.* **121**, 5221 (2004).
6. J. E. Butler, G. M. Jursich, I. A. Watson, and J. R. Wiesenfeld, *J. Chem. Phys.* **84**, 5365 (1986).
7. K. Mikulecky and K.-H. Gericke, *J. Chem. Phys.* **96**, 7490 (1992).
8. J. Klos and M. H. Alexander (manuscript in preparation).
9. A. Khachatrian and P. J. Dagdigian, *Chem. Phys. Lett.* **415**, 1 (2005).
10. S. Y. Lin, H. Guo, P. Honvault, and D. Xie, *J. Phys. Chem. B* **110**, 23641 (2006).
11. A. Khachatrian and P. J. Dagdigian, *J. Phys. Chem. A* **110**, 3388 (2006).
12. T. L. Myers, N. R. Forde, B. Hu, D. C. Kitchen, and L. J. Butler, *J. Chem. Phys.* **107**, 5361 (1997).
13. A. U. Grunewald, K.-H. Gericke, and F. J. Comes, *J. Chem. Phys.* **89**, 345 (1988).
14. R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkins, M. J. Rossi, and J. Troe, *Atmos. Chem. Phys.* **4**, 1461 (2004) <<http://www.iupac-kinetic.ch.cam.ac.uk/index.html>>.
15. M. J. Howard and I. W. M. Smith, *J. Chem. Soc. Faraday Trans. 2* **77**, 997 (1981).
16. R. Guadagnini, G. C. Schatz, and S. P. Walch, *J. Chem. Phys.* **102**, 774 (1995).
17. I. B. Pollack, Y. X. Lei, T. A. Stephenson, and M. I. Lester, *Chemical Physics Letters* **421**, 324 (2006).
18. P. A. Cleary, L. Dempsey, C. Murray, M. I. Lester, J. Klos, and M. H. Alexander, *J. Chem. Phys.* **XX**, YYY (2007).
19. B. C. Hoffman and D. R. Yarkony, *J. Chem. Phys.* **113**, 10091 (2000).
20. M. A. A. Clyne and W. S. Nip, in *Reactive Intermediates in the Gas Phase*, edited by D. W. Setser (Academic, New York, 1979), p. 2.
21. W. K. Bischel, B. E. Perry, and D. R. Crosley, *Chem. Phys. Lett.* **82**, 85 (1981).
22. J. Bittner, K. Kohse-Hoinghaus, U. Meier, and Th. Just, *Chem. Phys. Lett.* **143**, 571 (1988).
23. Y.-L. Huang and R. J. Gordon, *J. Chem. Phys.* **97**, 6363 (1992).
24. A. D. Tserepi, E. Wurzburg, and T. A. Miller, *Chem. Phys. Lett.* **265**, 297 (1997).
25. A. O'Keefe and D. A. G. Deacon, *Rev. Sci. Instrum.* **59**, 2544 (1988).
26. G. Berden, R. Peeters, and G. Meijer, *Int. Rev. Phys. Chem.* **19**, 565 (2000).
27. A. Teslja and P. J. Dagdigian, *Chem. Phys. Lett.* **400**, 374 (2004).
28. W. L. Wiese, J. R. Fuhr, and T. M. Deters, *Atomic Transition Probabilities of Carbon, Nitrogen, and Oxygen: A Critical Data Compilation*, *J. Phys. Chem. Ref. Data Monograph* **7** 1996).
29. Q. Wang and M. H. Alexander, *J. Chem. Phys.* **123**, 134319 (2005).
30. J. H. Reho, U. Merker, M. R. Radcliff, K. K. Lehmann, and G. Scoles, *J. Phys. Chem. A* **104**, 3620 (2000).
31. A. Nakayama and K. Yamashita, *J. Chem. Phys.* **114**, (2001).
32. T. Nakatsukasa, K. Yabana, and G. F. Bertsch, *Phys. Rev. A* **65**, 032512 (2002).
33. A. Vegiri, M. H. Alexander, S. Gregurick, A. McCoy, and R. B. Gerber, *J. Chem. Phys.* **100**, 2577 (1994).
34. M. H. Alexander, M. Yang, A. Walton, X. Yang, E. Hwang, and P. J. Dagdigian, *J. Chem. Phys.* **106**, 6320 (1997).
35. J. R. Krumrine, S. Jang, M. H. Alexander, and G. A. Voth, *J. Chem. Phys.* **113**, 9079 (2000).
36. D. T. Miriganian, M. H. Alexander, and G. A. Voth, *Chem. Phys. Lett.* **365**, 487 (2002).
37. L. C. Balling and J. J. Wright, *J. Chem. Phys.* **79**, 2941 (1983).
38. D. M. Ceperley, *Rev. Mod. Phys.* **67**, (1995).

- 39. M. Lax, J. Chem. Phys. **20**, 1752 (1952).
- 40. E. Cheng and K. B. Whaley, J. Chem. Phys. **104**, 3155 (1996).
- 41. Q. Hui, J. L. Persson, J. H. M. Beijersbergen, and M. Takami, Z. Phys. B **98**, 953 (1995).
- 42. M. E. Fajardo, S. Tam, T. L. Thompson, and M. E. Cordonnier, Chem. Phys. **189**, 351 (1994).
- 43. Q. Wang, M. H. Alexander, and J. R. Krumrine, J. Chem. Phys. **117**, 5311 (2002).
- 44. Q. Wang and M. H. Alexander, J. Chem. Phys. **124**, 034502 (2006).
- 45. M. H. Alexander, D. E. Manolopoulos, and H. J. Werner, J. Chem. Phys. **113**, 11084 (2000).
- 46. M. H. Alexander, J. Chem. Phys. **108**, 4467 (1998).
- 47. M. R. Hoffman and G. C. Schatz, J. Chem. Phys. **113**, 9456 (2000).
- 48. M. H. Alexander, G. Capecchi, and H.-J. Werner, Science **296**, 715 (2002).

III. LIST OF PUBLICATION PREPARED UNDER AFOSR GRANT NOS. FA9550-04-1-0152 AND FA9550-04-1-0103

1. A. Teslja and P. J. Dagdigian, "Determination of Oxygen Atom Concentrations by Cavity Ring-Down Spectroscopy," Chem. Phys. Lett. **400**, 374-378 (2004).
2. A. Khachatrian and P. J. Dagdigian, "Vibrational Relaxation of OH by Oxygen Atoms," Chem. Phys. Lett. **415**, 1-5 (2005)..
3. Q. Wang and M. H. Alexander, "Path integral Monte Carlo simulation of the absorption spectra of an Al atom embedded in helium," J. Chem. Phys. **123**, 134319 (2005).
4. S. Atahan and M. H. Alexander, "Coupled-States Statistical Investigation of Vibrational and Rotational Relaxation of OH($X^2\Pi$) by Collisions with Atomic Hydrogen," J. Phys. Chem. A **110**, 5436-5445 (2006).
5. A. Khachatrian and P. J. Dagdigian, "The effect of vibrational excitation on the collisional removal of free radicals by atoms: OH($v=1$) + N," J. Phys. Chem. A **110**, 3388-3392 (2006).
6. Q. Wang and M. H. Alexander, "Path integral Monte Carlo simulation of the recombination of two Al atoms embedded in *para*-hydrogen," J. Chem. Phys. **124**, 034502 (2006).
7. P. A. Cleary, L. Demsey, C. Murray, M. I. Lester, J. Kłos, and M. H. Alexander, "Electronic Quenching of OH $A^2\Sigma^+$ Radicals in Single Collision Events with Molecular Hydrogen: Quantum State Distribution of the OH $X^2\Pi$ Products from the Inelastic Channel." J. Chem. Phys. **126**, 204316 (2006).

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